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0-89 Transient Resonance Raman Scattering in Intermediately Coupled Localized Electron-Phonon System

—Frank-Condon like Excitation—

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Abstract

How the uncertainty relation in the transient resonance Raman scattering plays important roles in the correlation between absorption and emission is demonstrated, by taking an example of a localized electron-phonon system with a local or pseudo-local phonon mode intermediately coupled to the electron. We consider only the Frank-Condon like excitation by an extremely short pulse compared with the relaxation time of the system.

A Preliminaries

Let us consider one impurity center in large crystal lattice whose electronic ground and excited states are represented by the hamiltonians H_g and H_e respectively. H_g is the lattice energy. The excitation energy $V \equiv H_e - H_g$ is composed of the Frank-Condon excitation energy $\langle V \rangle \equiv T_r(\rho_g V)$ and the electron-phonon interaction δV;

$$V \equiv H_e - H_g \equiv \langle V \rangle + \delta V, \tag{1}$$

where $\rho_g \equiv \exp(-H_g/k_BT)/Tr[\exp(-H_g/k_BT)]$. The two electronic states $|g\rangle$ and $|e\rangle$ are supposed to be connected only through the radiative interaction Π_q. In R. R. S., we can assume that the electronic matrices $M_1 \equiv \langle g|\Pi_1|e\rangle$ and $M_2 \equiv \langle g|\Pi_2|e\rangle$ are independent of the vibrational coordinates (Condon approximation). Further, the radiative damping operator $\Gamma^{(0)}$ may be put to be a constant γ. In the case where the vector potential of the incident pulse is given by

$$A(r,\ t) = A_1 e_1 \phi_{k_1}(t - k_1 \cdot r/\omega_1) e^{-i(\omega_1 t - k_1 \cdot r)}$$

and the way of observation is specified by the mean frequency ω_2 of emitted photons and the coherence time Δt_c of a spectrometer, the time-resolved emission spectrum can be written in the form[1]

$$S(\omega_1,\ \omega_2;\ t,\ \Delta t_c) = \frac{|M_1 M_2^*|^2}{\Delta t_c} \int_{-\Delta t_c}^{\Delta t_c} d\mu \int_{-\Delta t_c + |\mu|}^{0} dm \int_{-\infty}^{t+m} ds \int_{-2(t+m-s)+\mu}^{2(t+m-s)+\mu} d\sigma\ e^{-2\gamma(t+m-s)} \cdot e^{-i\omega_1\sigma + i\omega_2\mu} \phi_{k_1}(s+\sigma/2)\phi_{k_2}^*(s-\sigma/2) \langle S_\mu^{(e)}(\tau') S_\sigma^\dagger \rangle, \tag{2}$$

where

$$\tau' = t + m - s + (\sigma - \mu)/2, \tag{3}$$

$$X^{(e)}(\tau) = e^{iH_e\tau} X e^{-iH_e\tau}, \tag{4}$$

and

$$S_\sigma^\dagger \equiv e^{i\sigma H_e} e^{-i\sigma H_g} = \exp_+\left[i\int_0^\sigma d\sigma_1 V^{(e)}(\sigma_1)\right], \tag{5}$$

$$S_\mu \equiv e^{i\mu H_g} e^{-i\mu H_e} = \exp_-\left[-i\int_0^\mu d\mu_1 V^{(e)}(\mu_1)\right], \tag{6}$$

After Toyozawa[2], we also define the instantaneous fluctuation by

$$\delta V_e(t) \equiv V^{(e)}(t) - \langle V^{(e)}(t) \rangle \tag{7}$$

and expand the logarithm of the correlator $\langle S_\mu^{(e)}(\tau') S_\sigma^\dagger \rangle$ in a power series of it. Within the second cummurant, this is given by

$$ln\langle S_\mu^{(e)}(\tau') S_\sigma^\dagger \rangle = i\int_0^\sigma d\sigma_1 V^{(e)}(\sigma_1) - i\int_0^\mu d\mu_1 V^{(e)}(\tau' + \mu_1) - \int_0^\sigma d\sigma_1 \int_0^{\sigma_1} d\sigma_2 \langle \delta V_e(\sigma_1)\delta V_e(\sigma_2)\rangle + \int_0^\sigma d\sigma_1 \int_0^\mu d\mu_1 \langle \delta V_e(\tau' + \mu_1)\delta V_e(\sigma_1)\rangle$$

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$$-\int_0^{\mu}d\mu_2\int_0^{\mu_2}d\mu_1<\delta V_e(\tau'+\mu_1)\delta V_e(\tau'+\mu_2)>. \quad (8)$$

O.L. from the relaxed excited state may be described by Eq. (8) more satisfactorily than by the alternative approximation of pair correlations in regard to $\delta V(t)$, except for the linear interaction (In this case, they agree to each other to give an exact expression.). In this paper, however, we suppose that the anharmonicity of the vibrations and relative variation of the elastic constants of the lattice in the electronic transitions are sufficiently small. Then, we may put

$$<\delta V_e(x)\delta V_e(y)>\simeq<\delta V\delta V(y-x)>$$
$$\equiv\int_{-\infty}^{\infty}d\omega\omega^2g(\omega)\{n(\omega)+1\}e^{i\omega(y-x)} \quad (9)$$

and

$$<V^{(e)}(x)>\simeq<V>+i\int_0^x dy<[\delta V,\ \delta V(y)]>, \quad (10)$$

where $n(\omega)\equiv[\exp(\omega/k_BT)-1]^{-1}$ and $g(\omega)$ is the so called "interaction spectrum" given by

$$g(\omega)=-g(-\omega)\equiv(2\pi)^{-1}\sum_i\omega_i\Delta_i^2\left\{\frac{\Gamma_i}{(\omega-\omega_i)^2+\Gamma_i^2}-\frac{\Gamma_i}{(\omega+\omega_i)^2+\Gamma_i^2}\right\}, \quad (11)$$

where i denotes vibrational normal (crystal ($i\neq0$) as well as local ($i=0$)) modes with the frequency ω_i, the reciplocal life time Γ_i and the shift of equilibrium position of normal coordinatee Δ_i.

As is well known, the interaction of the system can be characterized by $g(\omega)$ or its transforms $G_{\pm}(\mu)$ and G(="interaction strength");

$$G_{\pm}(\mu)\equiv\int_0^{\infty}d\omega\ g(\omega)\left|\begin{matrix}n(\omega)+1\\ n(\omega)\end{matrix}\right|\exp(\pm i\omega\mu) \quad (12)$$

and

$$G\equiv G_+(0)+G_-(0)=\int_0^{\infty}d\omega\ g(\omega)\{2n(\omega)+1\}. \quad (13)$$

According as the electron-phonon coupling is weak ($G\ll1$) or strong ($G\gg1$), the intermediate state after excitation is modurated rapidly or slowly. In this paper, we investigate only the case of intermediate coupling, i. e. hereafter we assume that

$$G\sim1. \quad (14)$$

B Frank-Condon like excitation

Modern laser technique has made possible to obtain an extremely short pulse with its width $\Delta_1^{-1}\sim10^{-13}$ sec which is much smaller than the mean period of vibration $2\pi/\bar{\omega}=10^{-11}\sim10^{-12}$ sec. Therefore, it would be meaningful to suppose such a way of excitation as

$$\phi_{k_1}(t_1)\phi_{k_1}^*(t_i)=\frac{1}{2\pi}\exp[-\Delta_1^2(t_1^2+t_i^2)/2]$$
$$=\frac{1}{2\pi}\exp[-2\Delta_1^2s^2-\Delta_1^2\sigma^2/2] \quad (15)$$

with the condition

$$\bar{\omega}[\equiv\text{the mean energy of phonon}]$$
$$\ll\Delta_1\ll<V>. \quad (16)$$

Then, Eq. (6) and (10) can be expanded in a power series of σ and s. Neglecting the terms of the order $(\bar{\omega}/\Delta_1)^nG\ll1$, $n=1, 2, \cdots\cdots$, under the conditions (14) and (16), we get

$$\ln<S_{\mu}^{(e)}(\tau')S_{\sigma}^{\dagger}>\simeq i\sigma<V>$$
$$-i\int_{-\mu/2}^{\mu/2}d\mu_1<V^{(e)}(t+m+\mu_1)>$$
$$-\int_0^{\mu}d\mu_2\int_0^{\mu_2}d\mu_1<\delta V\delta V(\mu_1)>. \quad (17)$$

Substituting Eqs (15) and (17) into (2) and performing the integrals over σ and s under the observation condition

$$t-\Delta t_c\gg\Delta_1^{-1}, \quad (18)$$

we have

$$S(k_1,\ k_2;\ t,\ \Delta t_c)\simeq\frac{\sqrt{2\pi}}{\Delta_1^2}|M_1M_2^*|^2\exp$$
$$\left[-2\gamma t+\frac{\gamma^2}{2\Delta_1^2}-\frac{(\omega_1-<V>)^2}{2\Delta_1^2}\right]F_e(k_2;\ t,\ \Delta t_c) \quad (19)$$

with

$$F_e(k_2;t,\ \Delta t_c)\equiv\frac{1}{2\pi\Delta t_c}\int_{-\Delta t_c}^{\Delta t_c}d\mu\int_{-\Delta t_c+|\mu|}^{0}dm\ e^{-2\gamma m}\exp[i\mu(\omega_2$$
$$-<V>_e)-G+G_+(\mu)+G_-(\mu)$$
$$-4i\int_{-\infty}^{\infty}d\omega\{n(\omega)+1\}g(\omega)\cos\omega(t+m)\sin(\omega\mu/2)], \quad (20)$$

here Eq. (17) was rewritten by the use of (9), (10) and (13). $<V>_e$ is the energy of the relaxed excited state;

$$<V>_e\equiv<V>-\int_0^{\infty}d\omega\ \omega g(\omega). \quad (21)$$

It is found that absorption and emission correlate

only through the last term in exp [……] in (20).

C C. A. E. via a local or pseudo-local mode

In the case of intermediate coupling, the most meaningful way of observation in order to study the dynamical aspect of vibrational relaxation would be

$$2\pi\omega_0^{-1}\ll\Delta t_c\ll t<\Gamma_0^{-1}<\gamma^{-1} \tag{22}$$

where ω_0 and Γ_0 are the frepuency of a local or pseudo-local mode and its reciplocal life time respectively. Then, from Eq. (11), the C. E. A. factor in the integrand of (20) can be written as

$$\begin{aligned}&\exp\Big[-4i\int_{-\infty}^{\infty}d\omega\{n(\omega)+1\}g(\omega)\cos\omega(t+m)\sin\frac{\omega\mu}{2}\Big]\\&\simeq\exp\Big[-4ig_0\sin\frac{\omega_0\mu}{2}\cos\omega_0(t+m)e^{-\Gamma_0 t}\Big]\\&=\sum_{n=-\infty}^{\infty}i^{|n|}J_{|n|}\Big(-4g_0\sin\frac{\omega_0\mu}{2}e^{-\Gamma_0 t}\Big)e^{i\omega_0(t+m)n}\end{aligned} \tag{23}$$

where $g_0\equiv\omega_0\Delta_0^2/2\sim1$ and $J_{|n|}(z)$ is the $|n|$-th order Bessel fuction;

$$J_{|n|}(z)=\sum_{k=0}^{\infty}\frac{(-1)^k(z/2)^{2k+|n|}}{k!\,(k+|n|)!} \tag{24}$$

The $n\neq0$ terms of Eq. (23) sinusoidally oscillate with high frequency of $n\omega_0\gg2\pi/\Delta t_c$ as the mean emission time $t+m$ lapses from $t-\Delta t_c$ to t, so that they are averaged to be negligible by performing the integral on m. Thus, substituting Eq. (23) into (20), we obtain

$$\begin{aligned}F_e(\omega_2;\ t,\ \Delta t_c)\simeq(2\pi)^{-1}&\int_{-\Delta t_c}^{\Delta t_c}d\mu\Big(1-\frac{|\mu|}{\Delta t_c}\Big)\ J_0\Big(-4g_0\sin\frac{\omega_0\mu}{2}e^{-\Gamma_0 t}\Big)\\&\cdot\exp[i\mu(\omega_2-\langle V\rangle_e)-G+G_+(\mu)+G_-(\mu)],\end{aligned} \tag{25}$$

For $\Gamma_0 t\gg1$, Eq. (25) approaches to O. L. spectrum, *i. e.* the intrinsic emission spectrum folded into the "U. P. broadening fuction";

$$F^{OL}(\omega_2,\ \Delta t_c)=\int_{-\infty}^{\infty}d\xi\ U(\xi)F_e(\omega_2+\xi) \tag{26}$$

with

$$\begin{aligned}U(\xi)&=(2\pi)^{-1}\int_{-\infty}^{\infty}d\mu\ e^{-i\xi\mu}\theta(\Delta t_c-|\mu|)\Big(1-\frac{|\mu|}{\Delta t_c}\Big)\\&=\frac{2\sin^2(\Delta t_c\xi/2)}{\pi\xi^2\Delta t_c}\end{aligned} \tag{27}$$

and

$$\begin{aligned}F_e(\omega_2)\equiv(2\pi)^{-1}&\int_{-\infty}^{\infty}d\mu\ \exp[i\mu(\omega_2-\langle V\rangle_e)\\&-G+G_+(\mu)+G_-(\mu)].\end{aligned} \tag{28}$$

In general, by the use of a frequency displacement operator $e^{i\omega_0\partial/\partial\omega_2}$, the time-resolved emission spectrum (25) can be expressed as

$$\begin{aligned}&F_e(\omega_2;\ t,\ \Delta t_c)\\&=J_0\Big(4g_0e^{-\Gamma_0 t}\sin\Big(\frac{\omega_0}{2}\frac{\partial}{\partial\omega_2}\Big)\Big)\cdot F^{OL}(\omega_2,\ \Delta t_c)\\&\equiv\sum_{k=0}^{\infty}\frac{1}{(k!)^2}\Big[g_0e^{-\Gamma_0 t}\Big\{\exp\Big(\frac{i\omega_0}{2}\frac{\partial}{\partial\omega_2}\Big)\\&-\exp\Big(-\frac{i\omega_0}{2}\frac{\partial}{\partial\omega_2}\Big)\Big\}\Big]^{2k}F^{OL}(\omega_2,\ \Delta t_c).\end{aligned} \tag{29}$$

The *k-th* term decays exponentially with the decay constant $2(k\Gamma_0+\gamma)$, and its emission spectrum is given by $\sum_{n=0}^{2k}\binom{2k}{n}(-1)^nF^{OL}(\omega_2+n\omega_0,\ \Delta t_c)$. If the $k>1$ terms as a whole are called as H.L. component, the negative H. L. spectrum must be regarded as back-absorption by the system. It is important to note that $F_e(\omega_2;\ t,\ \Delta t_c)$ is independent on Δt_c except for an insignificant feature that the widths of optical phonon side bands in $F^{OL}(\omega_2,\ \Delta t_c)$ are of the order of $(\Delta t_c)^{-1}$ instead of the intrinsic order Γ_0. However, Δt_c has implicitely played a constuctive role via the coherent average over the emission time $t+m$.

References

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